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Silicate-Nitrate Compounds: High-Pressure Synthesis and Stability of a Nitrate Scapolite

JULIAN R. GOLDSMITH, ROBERT C. NEWTON, AND PAUL B. MOORE

*Department of the Geophysical Sciences, University of Chicago,
Chicago, Illinois 60637*

Abstract

The compound $3\text{NaAlSi}_3\text{O}_8 \cdot \text{NaNO}_3$ has been prepared from crystalline albite and molten NaNO_3 in the temperature range $600^\circ\text{--}900^\circ\text{C}$ and at pressures above 7 kbar. Well formed crystals giving sharp single-crystal diffraction spots are tetragonal, $I4/m$, have the scapolite structure, and unit cell constants $a = 12.1643 \pm 0.0008 \text{ \AA}$, $c = 7.5297 \pm 0.0011 \text{ \AA}$. Density measured by a sink-float method is 2.618 ± 0.010 , slightly greater than that calculated from the cell constants, 2.598. An IR absorption spectrogram shows a strong maximum at 7.15μ uniquely assignable to the asymmetric stretching vibration of the nitrate groups.

Some of the relevant P - T relations in a portion of the system $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-N}_2\text{O}_5$ were explored. At higher temperatures or at lower pressures the nitrate scapolite breaks down to albite plus nitrate melt, and at still higher temperatures the compound $3\text{NaAlSiO}_4 \cdot \text{NaNO}_3$ (nitrate cancrinite) is formed along with a silicate melt and vapor produced by the decomposition of NaNO_3 . The cancrinite is quite refractory, persisting to temperatures near 1200°C at 15 kbar.

Although the P - T conditions for nitrate scapolite and cancrinite are such that stability in the deep crust and upper mantle is reasonable, it is unlikely that the requirement of an adequately oxidizing environment for the stability of any nitrate could be met.

Introduction

The minerals of the scapolite and the cancrinite groups are related in that they contain anionic radicals such as CO_3^{2-} , SO_4^{2-} , Cl^- in alkali and alkaline-earth aluminosilicate framework structures. For example, the idealized end-member compositions for scapolite are usually represented by $3\text{NaAlSi}_3\text{O}_8 \cdot \text{NaCl}$ [marialite] and $3\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot \text{CaCO}_3$ [meionite] (Shaw, 1960a, 1960b; Evans, Shaw, and Haughton, 1969). An idealized end-member cancrinite can be written as $3\text{NaAlSiO}_4 \cdot \text{CaCO}_3$ (Edgar, 1964). We have found no references in the literature to any aluminosilicates containing nitrate groups. The only nitrogen-containing silicates that we are aware of are ammonium-bearing feldspar (Erd *et al.*, 1964; Barker, 1964), and ammonium-bearing mica (Eugster and Munoz, 1966) in which NH_4^+ ion replaces K^+ in the structures. Little if any work on combined silicate-nitrate systems has been done, possibly because of the problem of decomposition of nitrates at moderate to high temperatures at atmospheric pressure. The 1969 supplement of the compilation of phase dia-

grams (Levin, Robbins, and McMurdie, editors) contains no references to such systems.

We have synthesized a nitrate scapolite ($3\text{NaAlSi}_3\text{O}_8 \cdot \text{NaNO}_3$) and a nitrate cancrinite ($3\text{NaAlSiO}_4 \cdot \text{NaNO}_3$) at high pressures and temperatures and have explored some of the relevant P - T relations in a portion of the system $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-N}_2\text{O}_5$.

Experimental Methods and Procedure

The starting materials for most of the runs were: (a) synthetic albite, crystallized hydrothermally at 700°C and 1 kbar H_2O pressure from a gel of the albite composition; (b) albite from Amelia Courthouse, Virginia; (c) a syngenetic K-feldspar (sanidine) from St. Peter Sandstone, Wisconsin; (d) reagent grade NaNO_3 and KNO_3 .

In several runs carnegeite was used, crystallized dry at 1270°C from a gel of the composition NaAlSiO_4 .

Mixtures of the feldspars and nitrates were sealed in platinum or gold capsules, generally in the ratio of one part silicate to one part nitrate by weight.

Later runs were all made with Na-feldspar and NaNO_3 , but some of the earlier runs contained mixtures of Na- and K-feldspars, and mixtures of NaNO_3 and KNO_3 , usually with a Na:K molar ratio of 3:1. The more complex compositions, containing both Na- and K-nitrates with Na- or K-feldspar or both, were used to investigate the possibility of locating the two limbs of the alkali feldspar solvus at elevated pressures and moderate temperatures by ion exchange between feldspars and molten nitrates. In runs of 1–2 kbar in cold-seal pressure vessels, alkali ion exchange was observed, although at the temperatures of most interest to us, below 500°C , little exchange took place in runs of several weeks. Furthermore, an "extraneous" phase subsequently identified as a cancrinite was observed to have formed in varying amounts in some of the runs. The exchange experiments were terminated at higher pressures in the piston-cylinder apparatus when it was observed that the nitrates reacted with the feldspars to produce cancrinite and scapolite structures.

Most of the runs were made in piston-cylinder units having 3/4 and 1 inch diameter bores with talc, NaCl, or glass used as the pressure-transmitting medium. Some of the experiments were carried out at 1 or 2 kbar in cold-seal pressure vessels. The sample geometry and pressure calibration methods used in the piston-cylinder runs were the same as described in Goldsmith and Newton (1969). The accuracy of the pressure calibration is illustrated by comparison with the results of Goldsmith and Newton on the calcite-aragonite transition with those determined in a gas pressure apparatus by Johannes and Puhan (1971, Fig. 5). The two sets of data agree within experimental error. Thus the error limits of pressure are believed to be ± 0.4 kbar at the temperatures of this study.

Temperature was measured in the piston-cylinder runs by chromel-alumel thermocouples in contact with the sample capsules. A thin film of alundum cement and a 0.002 inch thick platinum sheet separated the thermocouple metal from the capsule. Temperature was controlled automatically during the runs, and quenching to below 100°C at the end of a run was accomplished in a few seconds by turning off the heater power.

The nitrates have very low melting points, and at all of the experimental temperatures the nitrates were liquid. Rather little pressure is required to prevent dissociation, and even at 1–2 kbar and

$600^\circ\text{--}700^\circ\text{C}$ no significant amount of vapor was evident; the capsules remain collapsed. Only at temperatures high enough to produce melting in the silicate was a vapor phase encountered.

Reaction of the nitrates with platinum at the temperatures of this study was obvious. A black reaction product developed on the inside of the capsules, but in the length of time of the runs was not severe enough to significantly weaken the capsule mechanically, nor did it appear to have any effect on the phase chemistry of the run products. No attempt was made to identify it. No reaction between the nitrates and gold was observed.

All quenched samples were scanned with a Norrelco X-ray diffractometer, using filtered Cu radiation, normally at $1/4^\circ$ per minute. A few selected crystals were examined by the Weissenberg technique, and in addition a Debye-Scherrer pattern was produced from these same single crystals in a Gandolfi camera. Some of the runs were also examined under the petrographic microscope. Quenched siliceous glass was easily identifiable as large shards under the binocular microscope. The presence of a vapor phase was obvious from puffing of the quenched capsule. Selected single crystals were analyzed with an ARL electron microprobe.

Experimental Results

Scapolite

Reaction of albite with molten NaNO_3 to produce the nitrate scapolite at elevated pressures takes place in a few days at 600°C . At $700^\circ\text{--}900^\circ\text{C}$ and pressures of 8–15 kbar, well-formed euhedral crystals of over 0.01 mm grow in several days. In most runs that produced scapolite the crystals were clearly visible under a binocular microscope in a matrix of quench-crystallized nitrate, and easily separated by dissolving the highly soluble nitrate in water. It is apparent from the relative slowness of the reaction and the size and euhedral nature of the crystals that the scapolite is grown from the nitrate melt. The melt dissolves the albite, and scapolite is precipitated as the more stable phase. The scapolite occasionally has difficulty in nucleating, for its development is somewhat capricious: in some duplicated runs, made under essentially identical conditions to those in which scapolite formed, scapolite failed to appear. In the absence of scapolite the albite remains apparently unreacted. This nucleation difficulty tended to disappear at temperatures

>700°C. It was also noted that the Amelia albite tended to react more slowly or less effectively than the synthetic albite. Table 1 contains the pertinent data.

Scapolite was not observed to form in any of the rod-bomb runs. Before the *P-T* stability field of the

TABLE 1. Experimental Data

Run No.	T, °C	P, kbar	Time, Hrs.	Starting Material*	Results**
4	400	1	358	Am Ab + KNO ₃	No significant reaction
9	500	1	428	Am Ab + 2KNO ₃	Slight ion exchange in Ab - very little reaction
18	500	1	336	San + 2NaNO ₃	Significant ion exchange
21	550	1	478	Am Ab + San + 2 3:1 Na:K(NO ₃)	Very slight ion exchange, trace of canc
7	600	1	336	Am Ab + 2KNO ₃	Microcline formed by ion exchange
16	600	1	336	Am Ab + San + NaNO ₃ + KNO ₃	Nearly complete exchange to intermediate feldspars
17	600	1	336	San + 2NaNO ₃	Ion exchanged to albite, + canc
20	600	1	478	Am Ab + San + 2 3:1 Na:K(NO ₃)	Partially exchanged feldspars + some canc
29	600	7	335	Syn Ab + Syn San + 3:1 Na:K(NO ₃)	Canc + scap + some sanidine
3	600	15	167	Am Ab + San + 3:1 Na:K(NO ₃)	K-rich feldspar + scap
5	600	15	161	Am Ab + KNO ₃	Microcline formed by ion exchange + scap
15	600	15	143	Am Ab + San + 3:1 Na:K(NO ₃)	Scap
19	600	15	146	Am Ab + NaNO ₃	Albite + some canc
22	600	15	239	Am Ab + KNO ₃	Ion exchange to microcline
24	600	15	139	Am Ab + KNO ₃ + scap (seed)	Ion exchange to microcline. No scap growth
28	600	15	215	Syn Ab + Syn San + 2 3:1 Na:K(NO ₃)	Scap + sanidine

* Am Ab = Amelia albite. Syn Ab = synthetic albite. San = natural (syngenetic) sanidine. Syn San = synthetic sanidine. Canc = nitrate cancrinite. Scap = nitrate scapolite. Unless otherwise indicated, starting materials were blended in equal amounts by weight. Where ratios are shown, mixtures are in molar quantities. For example, Syn Ab + Syn San + 2 3:1 Na:K(NO₃) is a mixture, by weight, of 1 part synthetic albite, 1 part synthetic sanidine, and 2 parts of a 3 to 1 molar mixture of NaNO₃ and KNO₃.

** Almost all of the runs contained more nitrate than required to form the scapolite (or cancrinite). Thus, all of the runs contained a nitrate melt, not indicated in the "results" column. In the case of runs 37, 45a, 44, and 36, immiscible nitrate and silicate melts were present.

TABLE 1, Continued

Run No.	T, °C	P, kbar	Time, Hrs.	Starting Material*	Results**
14	600	20	68	Am Ab + 3:1 Na:K(NO ₃)	Scap
34	700	2	166	Syn Ab + NaNO ₃	Albite + canc
41a	700	8	70	Syn Ab + Scap (Run 35) + NaNO ₃	Scap + canc
41b	700	8	70	Syn Ab + NaNO ₃	Scap + canc
30	700	15	70	Syn Ab + Syn San + 2 3:1 Na:K(NO ₃)	Scap + some Na-containing sanidine
31	700	15	72	Syn Ab + NaNO ₃	Scap + some canc
32	700	15	94	Syn Ab + NaNO ₃	Scap + some canc
33	700	15	78	Am Ab + NaNO ₃	Albite + some canc
40	800	8	67	Syn Ab + scap (Run 35) + NaNO ₃	Albite + canc
42	800	8	43	2 Carnegieite + NaNO ₃	Canc (+ cubic phase)
38	900	8	78	Am Ab + NaNO ₃	Albite + some canc
39	900	8	43	Syn Ab + scap (Run 35) + NaNO ₃	Albite + canc
46a	900	11	24	3:1 Syn Ab: NaNO ₃	Albite
46b	900	11	24	Syn Ab + NaNO ₃	Albite
35a	900	15	43	Syn Ab + NaNO ₃	Scap
35b	900	15	43	Am Ab + NaNO ₃	Scap + some canc
37	1000	8	70	Am Ab + NaNO ₃	Silicate glass + canc + vapor
43a	1000	15	3	3:1 Syn Ab: NaNO ₃	Albite + canc
43b	1000	15	3	Syn Ab + NaNO ₃	Albite + canc
45a	1000	15	24	3:1 Syn Ab: NaNO ₃	Albite + trace glass + vapor
45b	1000	15	24	quartz + NaNO ₃	Apparently unchanged
44	1100	15	2	Syn Ab + NaNO ₃	Silicate glass + canc + vapor
36	1200	15	6	Am Ab + NaNO ₃	Silicate glass + vapor

nitrate scapolite was determined, its absence could be ascribed to the nucleation difficulty. As will be seen, however, it is more likely that scapolite is unstable relative to the albite and NaNO_3 in at least some of the relatively low-pressure rod-bomb runs.

The well-formed euhedral crystals (from run #14) have typical scapolite morphology; tetragonal, prismatic, with pyramidal terminations. They produce sharp single-crystal diffraction spots with tetragonal $I4/m$ symmetry; the pattern is that of the scapolite structure. The unit cell constants $a = 12.1643 \pm 0.0008 \text{ \AA}$, $c = 7.5297 \pm 0.0011 \text{ \AA}$ were obtained by 2 cycles of computer least-square refinement (Burnham, 1962) taken from X-ray powder diffractometer data. The unit cell volume is $1114.166 \pm 0.177 \text{ \AA}^3$. The density, measured by a sink-float method, is 2.618 ± 0.010 , slightly greater than that calculated from the cell constants, 2.598. This may reflect slight deviation from the assumed ideal formula.

The measured refractive indices are $\epsilon = 1.522 \pm 0.002$, and $\omega = 1.540 \pm 0.002$. A Gladstone-Dale calculation (Larson and Berman, 1934), using the ideal formulation as the basis for the specific refractive energies, gives a refractive index of 1.541, compared to the observed mean index of 1.534.

Several electron microprobe analyses were made on different crystals, pressed into indium metal. The analyses were carried out on the unpolished original crystal faces. The results in wt percent are:

	Na_2O	K_2O	Al_2O_3	SiO_2	N_2O_5
Ideal composition	14.22	0	17.55	62.03	6.20
As analyzed	11.02	0.06	18.00	53.99	—

The analyzed crystals were also from run #14, and thus crystallized from a melt containing potassium. There appears to be little if any potassium in the scapolite, although the surrounding indium metal may have interfered somewhat with the K analysis. Indeed, the low sum of the elements recorded may also be due to beam overlap onto indium. The low Na can be explained by Na volatile loss, for the NaNO_3 -containing scapolite is quite Na-rich. The slight excess of Al_2O_3 and the deficiency in SiO_2 compared to the ideal ($3\text{NaAlSi}_3\text{O}_8 \cdot \text{NaNO}_3$) composition may be real.

An IR absorption spectrogram shows a strong maximum at 7.15μ which is uniquely assignable to the asymmetric stretching vibration of the nitrate groups.

Cancrinite

In a number of runs in which scapolite was formed several extraneous X-ray diffraction lines were observed. This additional phase appeared more abundantly in some of the higher temperature runs, particularly in the absence of scapolite. Perusal of the ASTM Index to the X-ray Powder Data File for a reasonable composition with the appropriate lines revealed a reference to the synthetic compound $3\text{NaAlSiO}_4 \cdot \text{Na}_2\text{CO}_3$, called natrodavynite by Edgar and Burley (1963). Edgar and Burley found that this composition crystallized with a cancrinite structure at temperatures below approximately 600°C in the pressure range of 10,000–30,000 psi, but as a high temperature modification that they considered to be cubic (nosean structure) above approximately 600°C . Synthesis from a starting mixture of NaAlSiO_4 and NaNO_3 (run 42, Table 1) indicates that the phase encountered here is a cancrinite-like compound, most probably of the composition $3\text{NaAlSiO}_4 \cdot \text{NaNO}_3$. Cancrinite was observed in some of the rod-bomb runs.

An X-ray diffractometer scan was made of the product of run #42, using Cu radiation with KBrO_3 as an internal standard, at $1/8$ degree per minute. An attempt to index the pattern on a hexagonal lattice indicated that the sample was in fact a mixture or intergrowth of hexagonal cancrinite and a related cubic substance. It is likely that these substances are polymorphic modifications (with many coincident X-ray reflections) of $3\text{NaAlSiO}_4 \cdot \text{NaNO}_3$, namely, a lower-temperature cancrinite form and a high-temperature cubic modification which are analogous to the natrodavynite-nosean pair discussed by Edgar and Burley (1963). We have not pursued the examination of this relationship, but it is possible that cancrinite forms during cooling of the run.

The fairly strong 111 and 400 reflections of the hexagonal cancrinite structure are not coincident with any reflections of the cubic phase, and yield lattice constants for the cancrinite of $a = 12.76_0$, and $c = 5.19_8$. In addition, the 310 reflection of the nosean structure is uniquely resolvable and gives $a = 9.05_1$.

Phase Relations on the Join $\text{NaAlSi}_3\text{O}_8$ - NaNO_3

The appearance of cancrinite in some of the runs made over much of the P - T range in this system requires an interpretation not immediately evident in the raw data. With this reservation the pertinent data from Table 1 are plotted in Figure 1, which

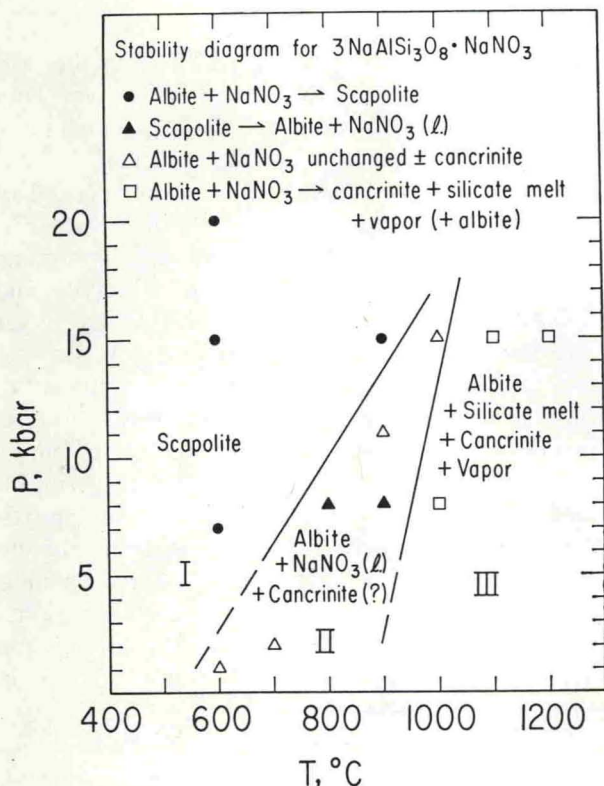


Fig. 1. P - T relations for the composition $3\text{NaAlSi}_3\text{O}_8 \cdot \text{NaNO}_3$.

is a P - T stability diagram for the join $\text{NaAlSi}_3\text{O}_8$ - NaNO_3 .

Three fields may be delineated for a bulk composition corresponding to the scapolite formula, $3\text{NaAlSi}_3\text{O}_8 \cdot \text{NaNO}_3$. Field I contains scapolite, field II contains the thermal decomposition products of scapolite, namely albite and nitrate melt (+ cancrinite?), and field III contains albite + silicate melt + vapor + cancrinite. There is some doubt about the stability of cancrinite, particularly in field II. If, however, there is considerably more NaNO_3 in the system than necessary to make scapolite, as was true in many of our runs, nitrate melt will be present in all three fields and will replace albite in field III.

The boundary between fields I and II is univariant and has been reversed (nos. 35a, 35b, 40, 41a, Table 1) at 8 kbar. In shorter runs (nos. 43a, 43b, Table 1) cancrinite appeared in field II. Because the silica content of cancrinite is lower than that of scapolite, it is obvious that a complementary amount of silica must have been stored elsewhere in the assemblage. No evidence for an additional silica-rich phase was found. Although the

most likely explanation is that it was dissolved in the nitrate melt, no evidence of high solubility was seen in the quenched charge of a run made with a mixture of quartz and NaNO_3 (no. 45b, Table 1). Likewise, in the somewhat analogous system $\text{NaAlSi}_3\text{O}_8$ - Na_2CO_3 at 1 kbar, the solubility of albite in molten Na_2CO_3 is very small (Koster van Groos and Wyllie, 1966). Longer runs on albite plus NaNO_3 at 15 kbar showed no cancrinite. The cancrinite formed in field II in shorter runs or at lower temperatures in rod bombs (nos. 17, 20, 21, 34, Table 1) would therefore appear to be a metastable phase possibly attended by metastably high solubility of SiO_2 . If so, the phase boundary between fields I and II can be considered to be doubly degenerate in the system Na_2O - Al_2O_3 - SiO_2 - N_2O_5 , being essentially the univariant dissociation of scapolite to albite plus molten NaNO_3 .

Cancrinite was found in the runs made below 1200°C in field III, and metastability is less likely at the higher temperatures of this field than in field II. If the cancrinite is stable in field III, the five phases along the II-III boundary satisfy univariacy in the four-component system. The siliceous melt was produced at temperatures as low as 1000°C . This strongly suggests that a considerable amount of Na_2O is added from the breakdown of nitrate. Further evidence for the enrichment of the silicate melt in Na_2O relative to albite comes from the refractive index (~ 1.52) of the glass from run no. 36 at 1200°C . The isofrac data from the system Na_2O - Al_2O_3 - SiO_2 (Schairer and Bowen, 1956) although uncorrected for the effects of temperature and pressure, would indicate a composition substantially enriched in Na_2O . The nitrogen liberated by the breakdown of NaNO_3 forms a vapor of the bulk composition N_2O_5 . The fact that a puffed capsule was always found in conjunction with identifiable siliceous glass is consistent with this picture.

The runs defining the field boundaries are widely spaced, and only the scapolite field boundary has been reversed, and only at one pressure. Therefore there is considerable uncertainty in the slope of the boundaries. It may be easily demonstrated that the experimental slope of the scapolite decomposition is essentially correct, however. Thus, if we take the density of the scapolite as 2.60 gm/cc , the molar volume is 335 cc/mole . The molar volume of molten NaNO_3 is the volume of the solid, 37.6 cc/mole (Robie and Waldbaum, 1968) plus the ΔV of fusion, which can be gotten from the entropy of fusion of

6.4 e.u. (Robie and Waldbaum, 1968) and the initial dP/dT melting slope of about 70 bars/°C (Klement and Jayaraman, 1966, p. 347). Ignoring thermal expansion corrections and using 100.2 cc/mole for albite, we get 7 cc/mole for the volume change of scapolite breakdown. The entropy change will be given as a first approximation by the heat of fusion of NaNO_3 . Thus $dP/dT \sim 6.4 \times 41.8/7 = 38$ bars/°C. The entropy change will be slightly larger than this because of the relatively large molar volume of the assemblage albite + NaNO_3 (Fyfe, Turner, and Verhoogen, 1958), which will increase the dP/dT slope by a small amount. If we used the physically measured density of 2.62 gm/cc for scapolite we would get a smaller slope. The slight solubility of albite in the nitrate melt is still another factor which has not been considered. Nevertheless, the general validity of the experimental slope is evident.

It is established that the nitrate scapolite is quite a refractory phase at high pressures. At still higher pressures, beyond the experimental range of this investigation, albite will be replaced as a scapolite decomposition product by jadeite plus quartz. The effect of albite breakdown on the scapolite stability is easily calculated. The boundary separating jadeite + quartz + nitrate melt from scapolite will be very nearly coincident with the albite to jadeite + quartz curve. This is a consequence of the fact that the ΔV of scapolite breakdown changes from small and positive to large and negative when jadeite + quartz becomes stable. This will be the case regardless of whether the I-II and II-III boundaries intersect before albite becomes unstable. Thus the field of stability of the scapolite will be essentially confined to the region where albite is stable.

The cancrinite appears to be thermally very stable. The present evidence indicates that it is absorbed into the siliceous melt between 1100°C and 1200°C at 15 kbar. Cancrinite by itself will be yet more thermally stable. Albite will also be progressively absorbed into the silicate melt as temperature is increased in field III.

Some Crystal-Chemical and Petrologic Considerations

At first glance one might discount the possible role of nitrate groups as significant elements in the structure of silicates. The structural similarity between crystalline NaNO_3 and CaCO_3 is well known,

however; NaNO_3 is basically the calcite structure type (Wyckoff, 1920), and the effective ionic radii are similar. The nitrate scapolite can be viewed as a NO_3 -containing marialite. It has a large field of stability, and can be appropriately considered a high-pressure phase. In fact, if the unusual compositional requirements could be met in the earth, this phase could exist as a mineral in the upper mantle. We have not investigated the stability relations of nitrate or nitrate-containing scapolites or cancrinites (or sodalite-nosean minerals) in chemical environments approaching rocks of the deep crust or upper mantle. However, it is unlikely that conditions in the deep earth are sufficiently oxidizing to make nitrates stable; aside from the essential range of stability with respect to P and T , the tendency for nitrate to be reduced is very great. Only locally and under rather unusual oxidizing conditions might nitrate minerals be stable.

We have not attempted the synthesis of any other mineral species in which NO_3 might replace CO_3 , nor have we attempted to replace some rather than all of the CO_3 with NO_3 in scapolite. This matter could be of importance in consideration of CO_2 and possibly N_2 stored in or derived from the mantle or deep crust. There is no information in the literature on analyses for nitrogen in scapolite or related minerals. Wlotzka (1961) reports N as NH_3 in a variety of rocks, but found no NO_3 -nitrogen in crustal rocks except for minute amounts (5-20 g/ton) in surface sediments, some saline clays, and limestones.

Shaw (1960b) points out that although scapolite is typically a metamorphic mineral, it coexists with a wide variety of common minerals and in a large number of rock types that probably formed over a large range of P and T conditions. That it is not an even more common mineral is probably because of compositional factors: the requisite anions usually are sparingly present in quartzo-feldspathic rocks, and any water present would probably form zoisite or mica at the expense of scapolite under most crustal conditions. The large P - T field of stability of the nitrate scapolite is less surprising in light of the cosmopolitan character of the natural scapolites. It was inferred from the present work on the nitrate scapolite that its upper pressure limit is nearly coincident with the upper pressure stability limit of albite. It may well be found that this upper pressure stability limit of natural scapolites will approximate that of the feldspars. Work on the upper pressure

limits of marialite and meionite is currently under way in this laboratory.

Similarly, the nitrate cancrinite is a very refractory phase, and it is probable that the typical carbonate cancrinites are more so. Edgar (1964) states, "The stability data indicate that the common varieties of cancrinite, namely the calcium carbonate and the sodium carbonate end members, are moderately high temperature minerals. The calcium carbonate and potassium carbonate varieties are reaction products of nepheline and the appropriate carbonate." As in scapolite, the availability of anions or anionic groups may restrict the occurrence of cancrinite; otherwise it might be more common, particularly in high-temperature metamorphic rocks.

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